A Possible Future for the Thermophysics of Fluids

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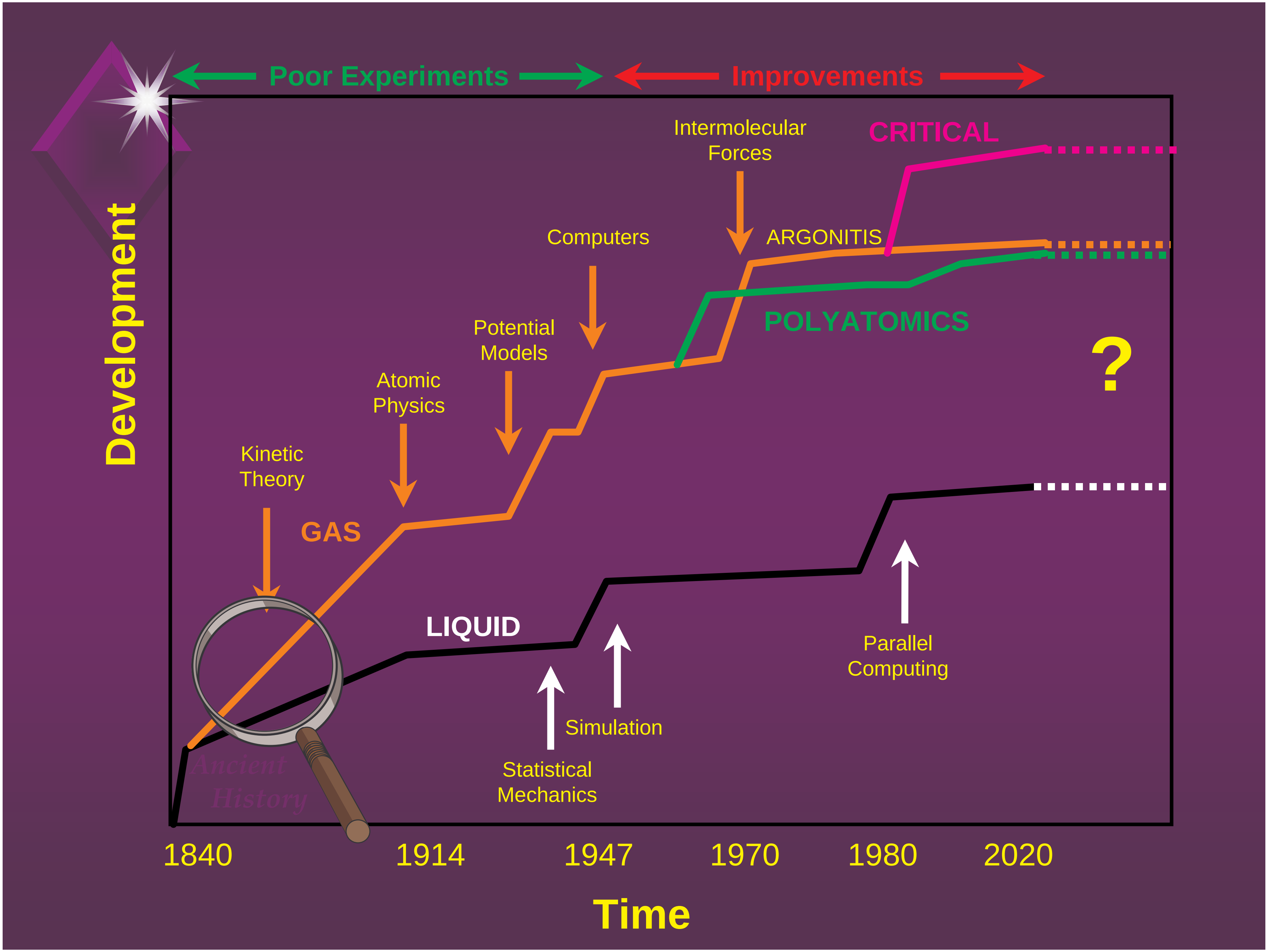
Intent

- **To stimulate discussion of the future role of research in the thermophysics of fluids by examining**
  - Beginning
  - Development
  - Present state
  - An analysis of present state
  - Various possible futures
- **A personal view biased on experience of**
  - Transport properties
  - Physics
  - Chemical Engineering
  - Wide perspective of research


Poor Experiments
Improvements
Development
Time
Kinetic Theory
Atomic Physics
Potential Models
Computers
Intermolecular Forces
GAS
ARGONITIS
CRITICAL
POLYATOMICS
?
LIQUID
Statistical Mechanics
Simulation
Parallel Computing
Ancient History
1840
1914
1947
1970
1980
2020

Ancient History

(largely experimental)

- 18th Century
  - Capillarity
- 19th Century
  - Liquefaction of gases
  - Rumford (1797) -Andrews (1869)
  - Critical point
  - Boyle’ Law
  - Charles Law
  - Deviations (Regnault)
  - Viscosity (Maxwell)

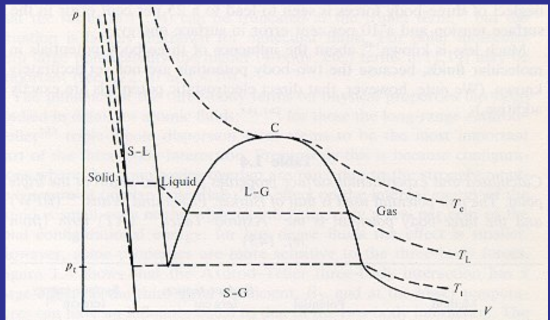
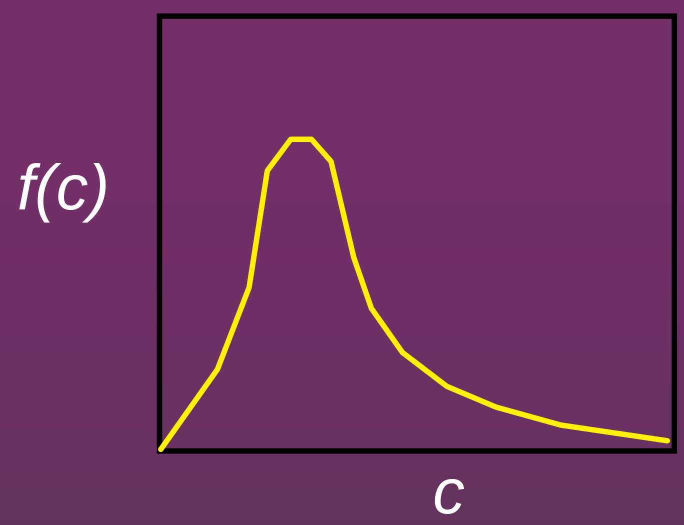


FIG. 1.5. p–V projection of the p–V–T diagram for a pure fluid. Solid lines are phase boundaries, dashed lines are isotherms, horizontal dashed lines are tie-lines connecting coexisting phases, p_t and T_t are triple-point pressure and temperature, and C is the gas–liquid critical point.

1

Ancient History
(largely theoretical)

- Clausius and Maxwell
  - Maxwellian distribution
  - transport of mass, energy momentum
  - Mean-free path
  - Virial theory
  - Van der Waals
  - Boltzmann
  - Corresponding states



1914-1949

(largely theoretical)

- The era of the gas
    - ‘A fallow period for liquids’ *Rowlinson*
  - Virial equation
  - Chapman-Enskog theory
  - Intermolecular potential models
      - Sutherland
      - Keesom
      - Lennard Jones
    - Second virial coefficient 1924
    - Viscosity 1942-1949
- Liquids neglected
    - simple theories

1914-1949

(largely experimental)

- Thermodynamic Properties
  - Traditional methodology
  - Careful manufacture
  - Great skill
  - Considerable time/continuity
  - Improving precision and accuracy
- Transport Properties
  - Traditional methodology
  - Simple instruments
  - Great skill
  - Ignorance of fluid mechanics
  - Static precision and accuracy

Transport Property Instruments

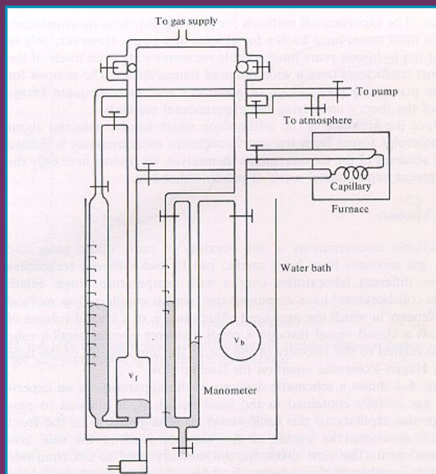


Fig. 6.4. A schematic diagram of a capillary viscometer.

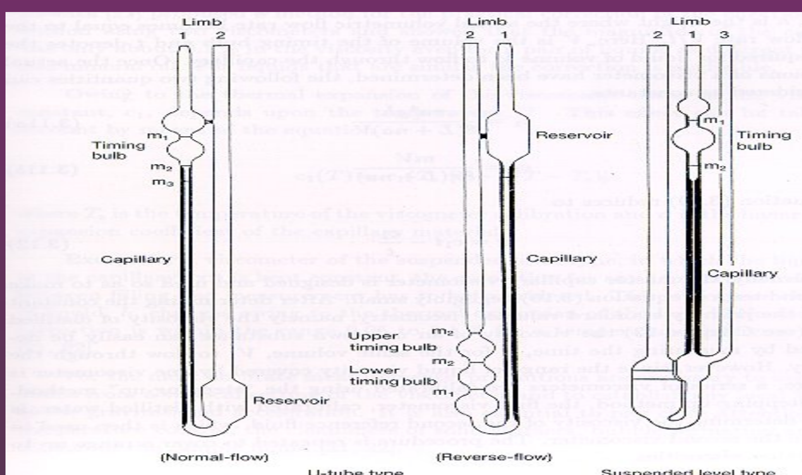


Figure 3.6 Capillary master viscometers.

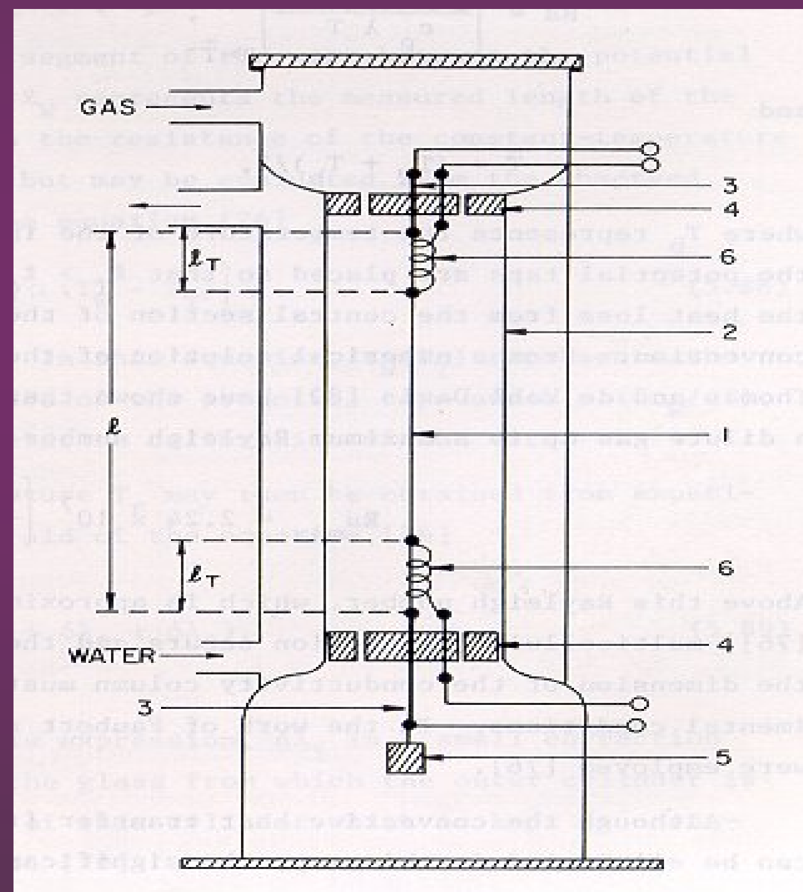


Figure 5.26. Thermal conductivity column instrument.

1945-1966

largely theoretical

- Liquids
  - Integral equations for Equilibrium
    - Kirkwood, Yvon Bogoliubov Born Green
  - Computer Simulation
    - Monte Carlo
      - Hard spheres (1950)
      - Lennard-Jones (1957)
    - Molecular Dynamics
      - Hard spheres (1956);
      - Lennard-Jones (1964)

Polyatomic gas transport properties

- Gases
  - Kinetic theory for polyatomic systems
    - Wang-Chang, Uhlenbeck, de Boer
  - Exact Calculation impossible even if
    - semiclassical
    - classical
  - Mason-Monchick approximate theories
    - Collision dynamics simplified
    - pseudo-spherical assumptions

1945-1966

(largely experimental)

- Engineers become involved
  - Steam a driving force
  - engineering design of equipment
  - decline of chemists
  - decline of glass apparatus
- Fluid mechanics
  - Navier-stokes equations
  - Analytic solutions of non-linear differential equations
  - Convection

Accurate Viscosity Measurements

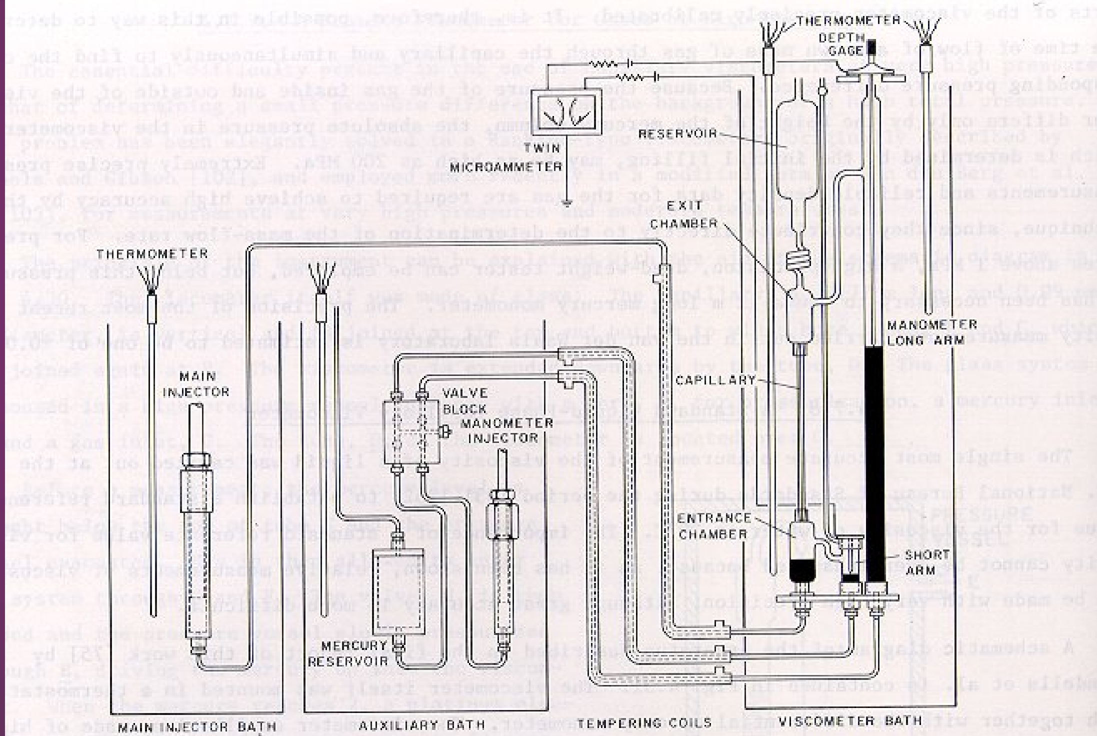
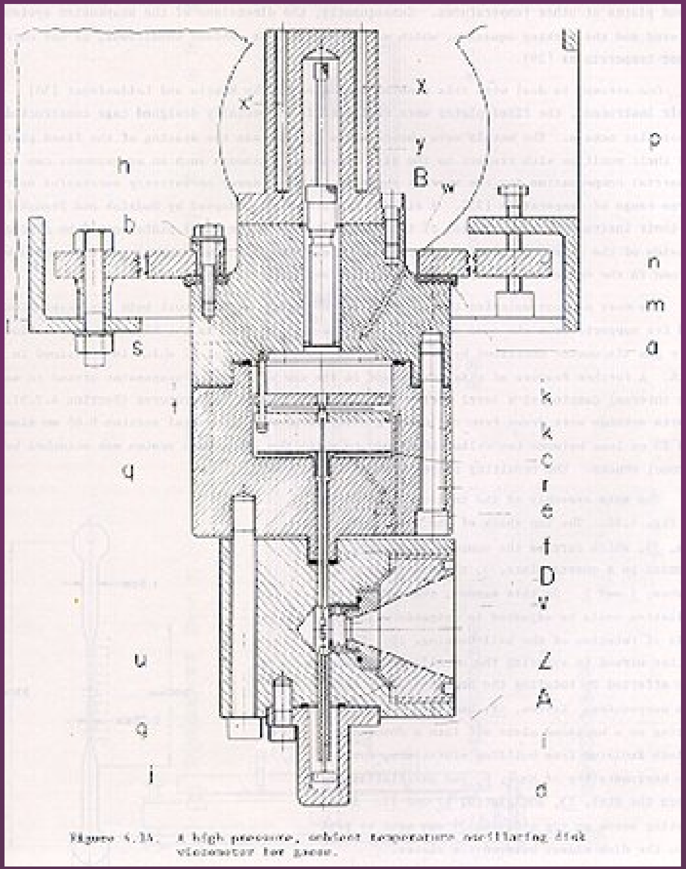


Figure 4.31. A schematic diagram of the capillary viscometer employed by Swindells and his collaborators for the determination of the viscosity of water at 20°C. (Taken from Swindells, Coe, and Godfrey, J. Res. Natl. Bur. Stand., 48, 1, 1952.)

1945-1966 (Largely Experimental)

- Careful, constrained design
  - construction
  - measured variables selected to allow high precision
  - metal has a role!



New viscometers

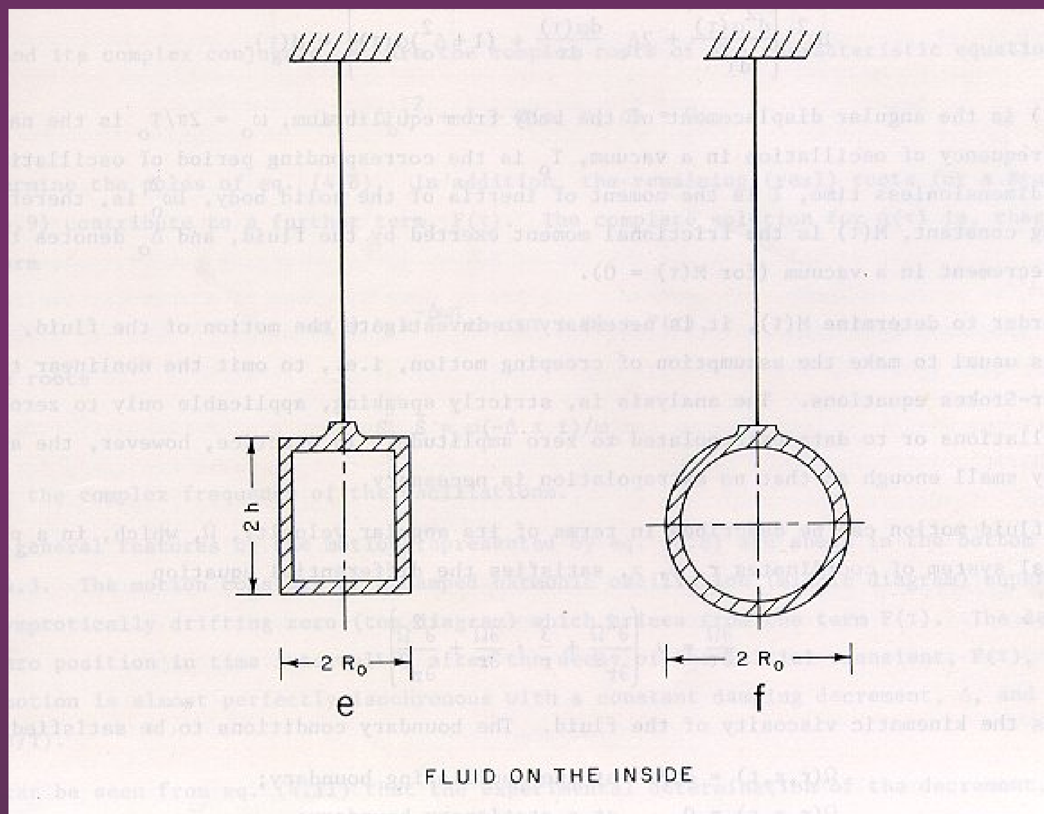


Figure 4.2. Oscillating-body viscometers - fluid internal to the oscillator.

1966-1975

(Experiment and theory)

- Intermolecular forces era
  - Molecular beam scattering
  - Infra-red spectroscopy on dimers
  - second virial coefficient
  - Noble gases
  - Exciting era
- Viscosity data inconsistent
  - New programme of measurement
    - Kestin, Smith

Molecular beam scattering

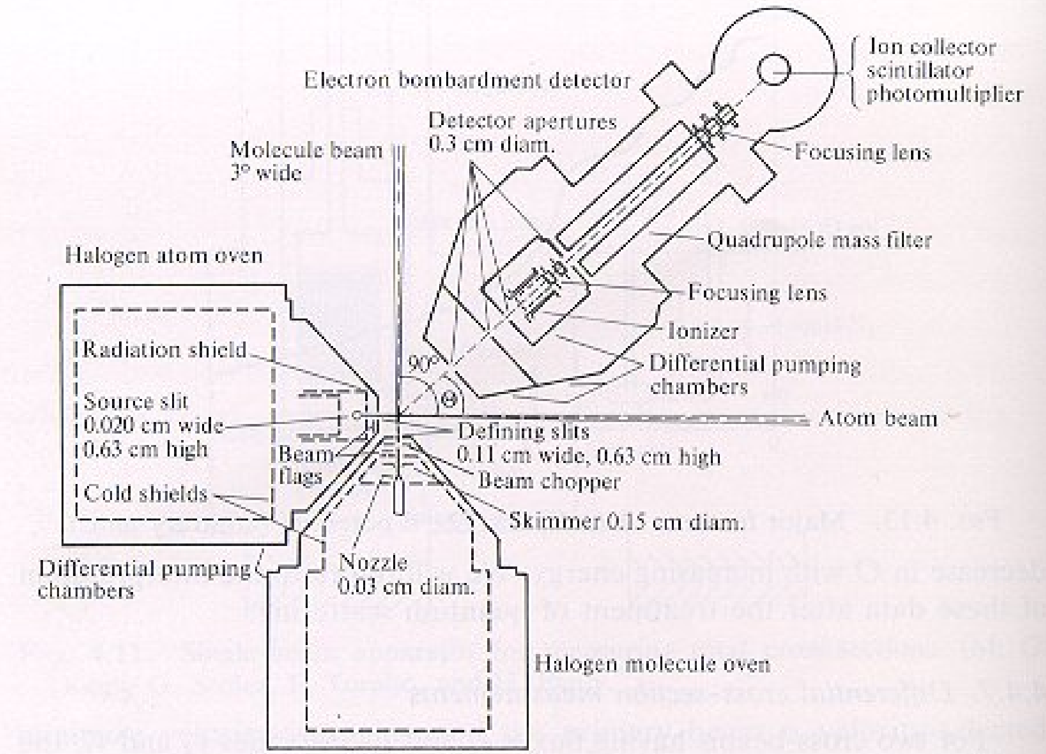


FIG. 4.14. Molecular beam apparatus for measuring differential cross-sections. (Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach.[24])

Molecular beam scattering

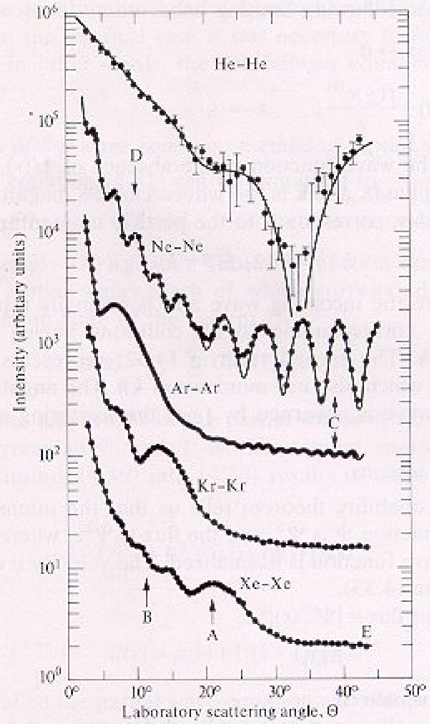


FIG. 4.15. Differential cross-sections $\sigma(\Theta, E)$ for the inert gases, He, Ne, Ar, Kr, and Xe, showing fine structure. Principal features: (A) rainbow maximum; (B) supernumary rainbow peaks; (C) symmetry (identical particle) oscillations; (D) high-frequency quantum oscillations; (E) monotonic large angle scattering. (J. M. Farrar, T. P. Schafer, and Y. T. Lee.[25])

Argon Intermolecular potential

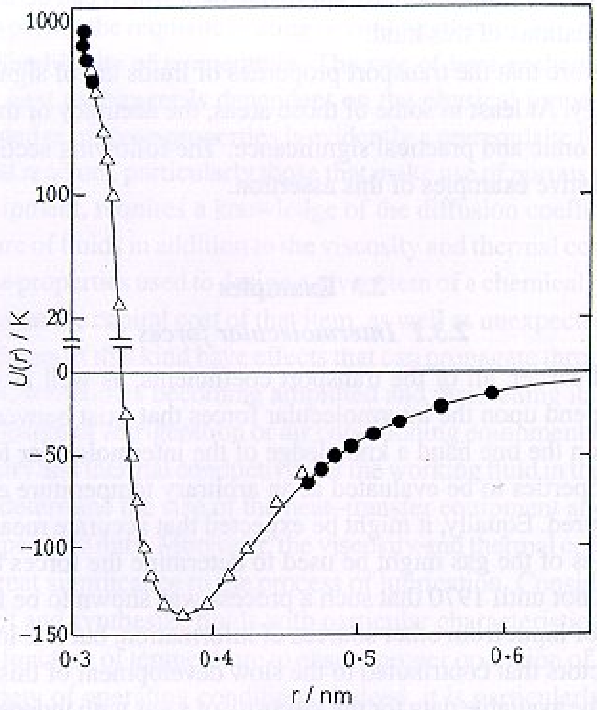


Fig. 2.1. A modern version of the intermolecular pair potential for argon. Solid line: a representation of the full potential; symbols: △ inversion of gas viscosity; ● inversion of second virial coefficient.

Intermolecular potentials

- Problem solved
  - New viscosity data accurate
  - All possible pairs, combinations of gases studied over a wide range of T
  - ONLY low pressure (density) data used
  - Inversion methods
  - Intermolecular potentials known for noble gases

Divergence (1975)

- Physics (Transport)
  - Dilute Polyatomic gases difficult
    - internal degrees of freedom
    - non-spherically symmetric potentials
  - But
    - Thermal conductivity is a new property
  - So approximate physics employed that was untested until 1990
    - Mason-Monchick approximation etc
    - Considerable misunderstanding

Divergence

- Critical behaviour of fluids
  - Entirely different type of physics
  - Intermolecular interactions not important
  - Entirely new types of experiment
- High density Fluids
  - Simulation
  - Long-time tails and logarithmic term
- Measurements (Achieving high accuracy)
  - Thermal conductivity
  - Viscosity
  - Diffusion

Thermal conductivity

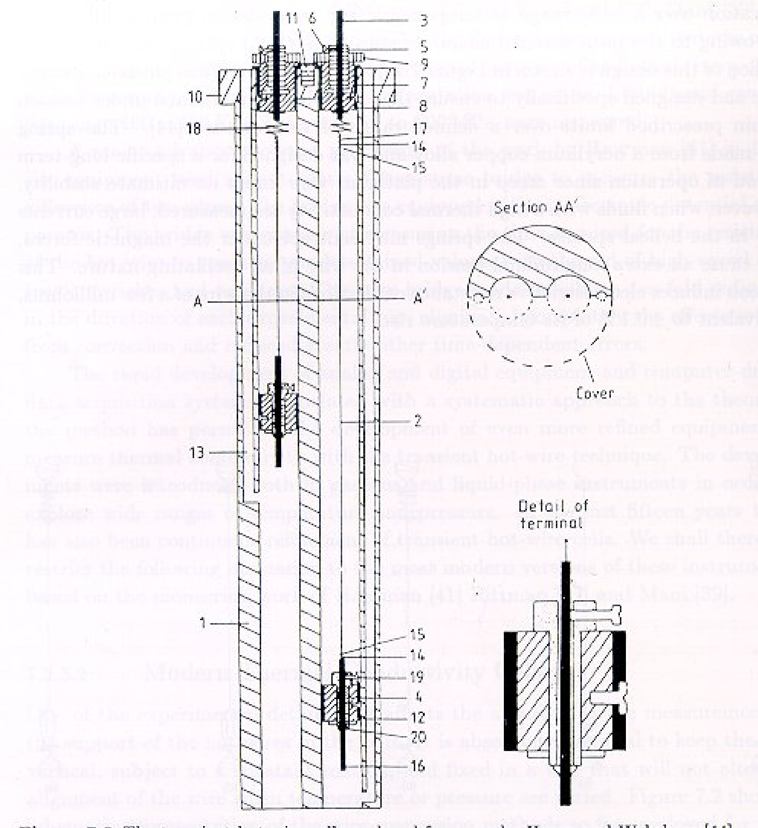
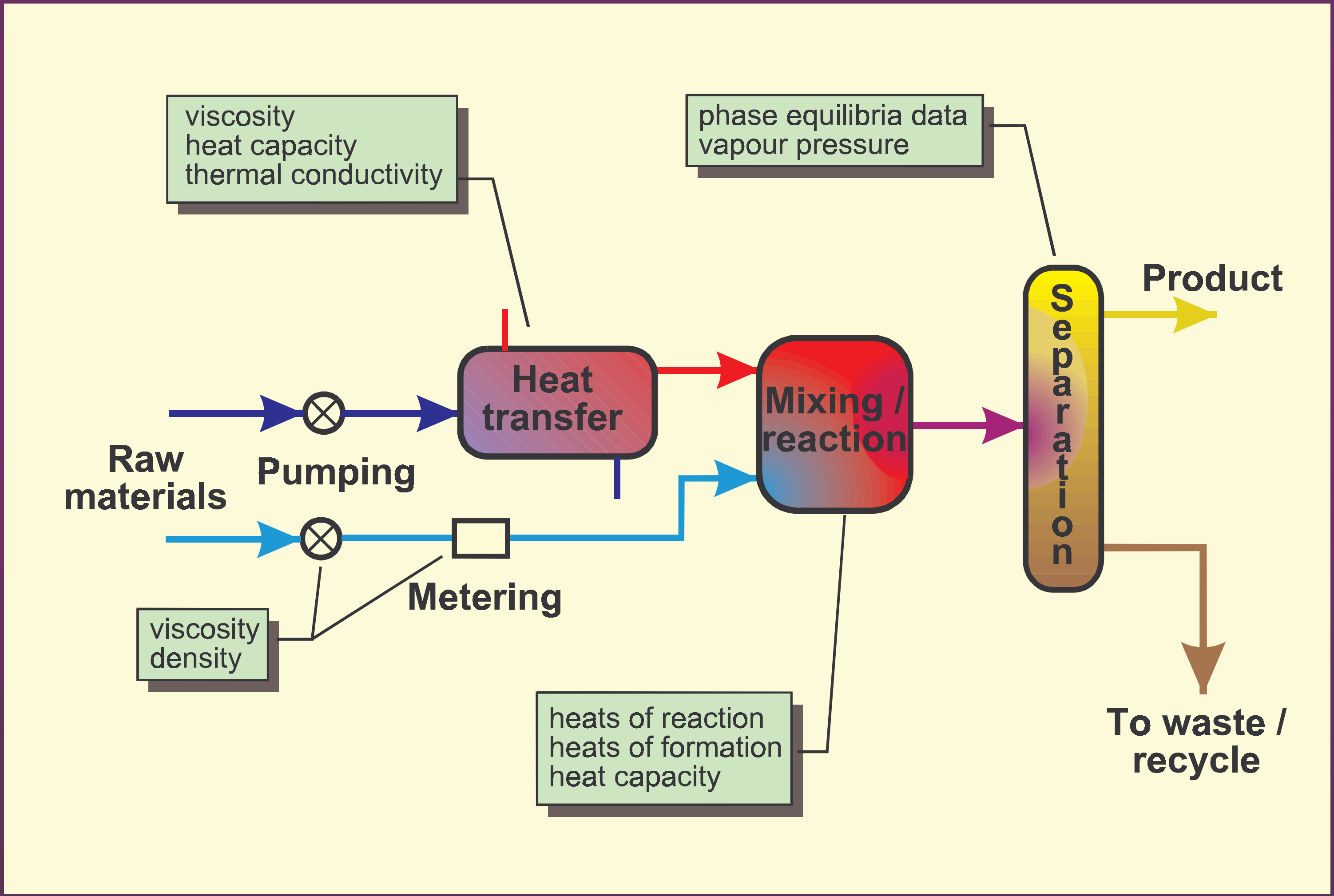


Figure 7.3 The transient hot-wire cell employed for gases by Haran and Wakeham [44].

Divergence

- Physics (Thermodynamics)
  - Pure Fluids
    - Computer simulation (Simple systems, simplified models of potential)
    - A variety of models of thermodynamics
    - Corresponding states even for non-spherical systems
    - Perturbation theory
    - Hard-sphere models
    - Critical behaviour of fluids

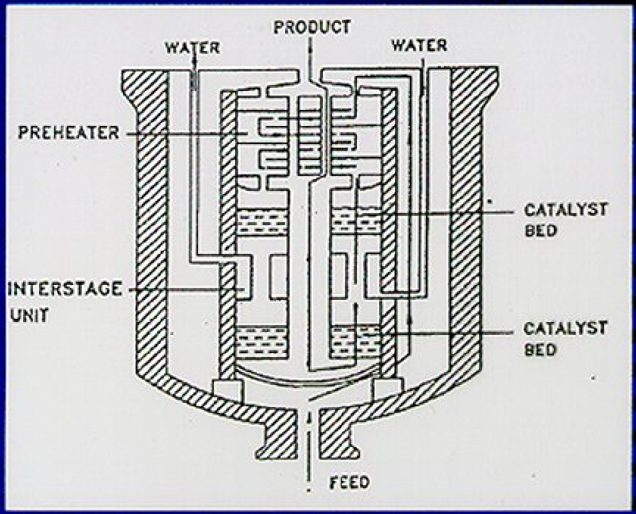
Process Engineering



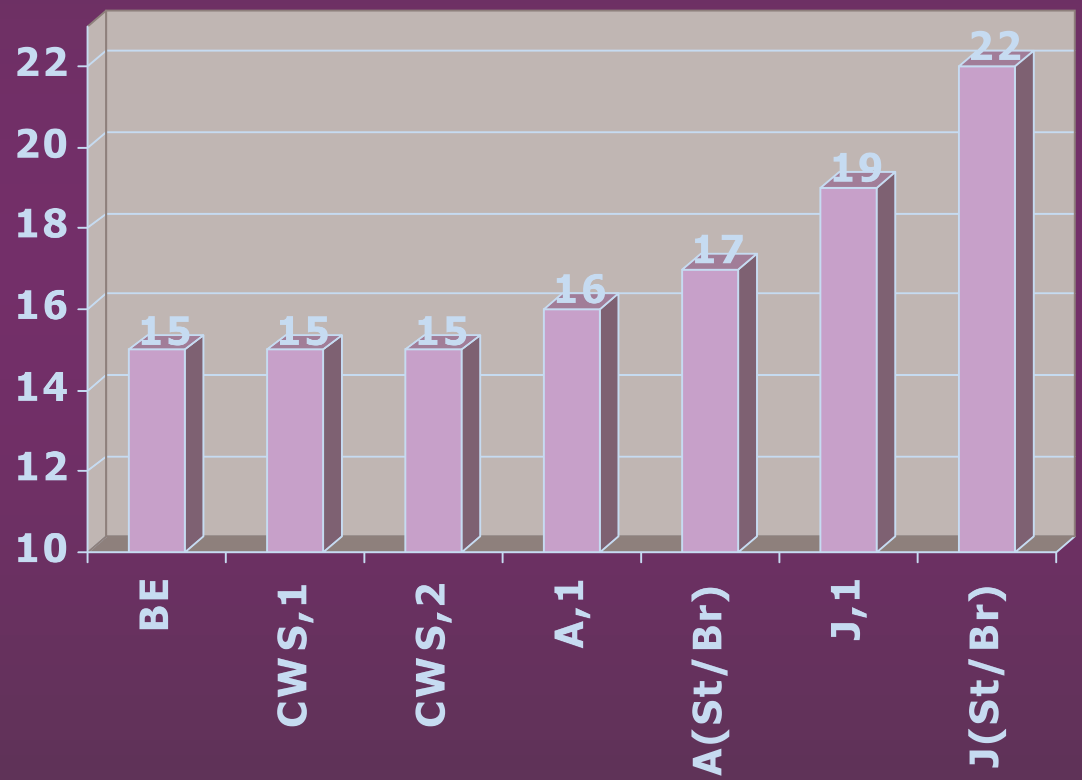
Engineering (Process)

- Design of processes becomes more computer-based
  - search for optimum design
    - energy efficiency
    - maximum profit
  - generated need for thermodynamic and transport properties in databases and representational equations
  - multicomponent systems over a wide range of conditions
  - phase behaviour most important
  - robust computation procedure vital

Methanol Synthesis Reactor



An illustration of effect of errors in simulations on design of a distillation column



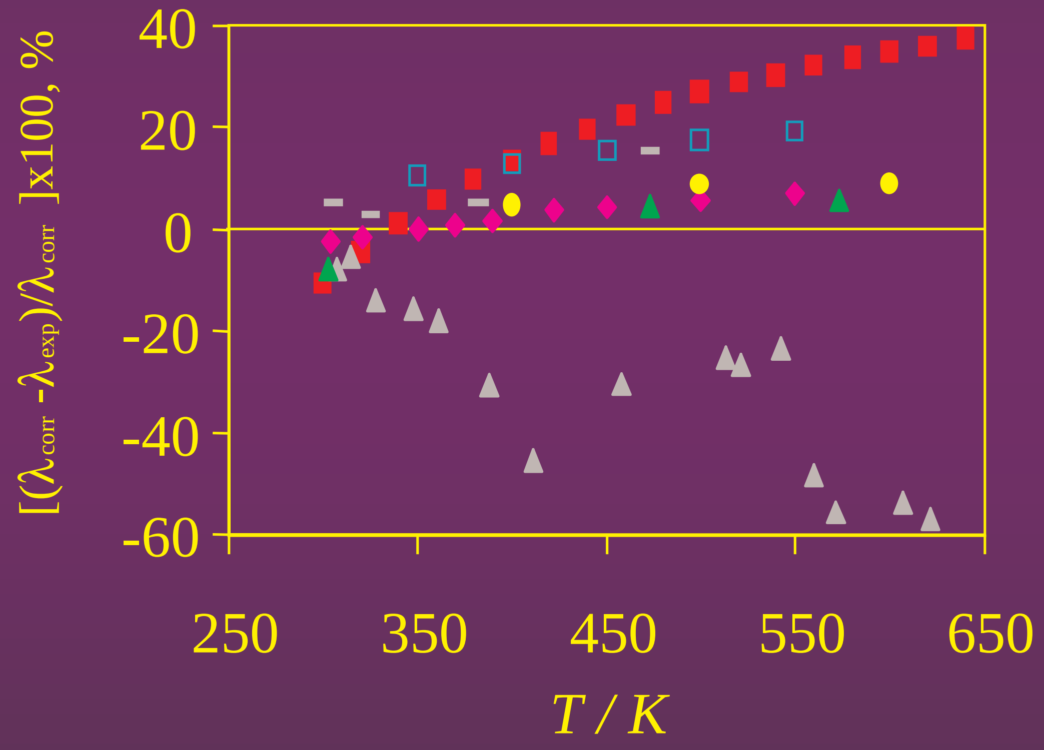
Engineering need dominates (1975-1999)

- Conflicts
  - Physics very difficult and not well-enough developed
  - Simulation promises, but cannot deliver for real systems
  - Experimentalists seek funding using an engineering justification but only short-term funding
  - Rapid results not available from precise experimental equipment that was used before
  - Rapid results require easily accessible conditions

A period of frustration

- Conflicts
  - rapid results mean pure fluids
  - Each thesis or proposal promises binary systems and possibly ternary, never delivers
  - rapid results obtained from different equipment than the accurate techniques and often wrong (R134a!)
  - Arguments for accurate measurements drowned by the need for speed and fitness for purpose

Thermal conductivity of Gallium



An age of frustration

- Industry cannot wait
  - IUPAC empirical equations of state, minimum theory, critical assessment of data for pure fluids
  - Corresponding states
    - One-fluid
    - Two-fluid
    - Kestin, Ro & Wakeham
  - Cubic equations of state
  - UNIFAC, UNIQUAC
  - Mixture rules, based on poor physics but what else can be done?

Process design

- Empirical correlations for properties dominate the software
- Exact theory fails : use what there is and avoid limitations
- Experiment fails to provide enough data
- Real systems too complicated (or dirty) to measure
- Delivery from accurate measurement supported by theory/semi-empiricism does not deliver
- Mixtures and liquids neglected
- Simulation begins to be a force

Experimentalists

- Concentration upon old techniques, simple fluids and a few mixtures
  - Volumes, enthalpies of mixing
  - Viscosity of simple liquids
  - Transport properties of environmentally-friendly refrigerants
- Blame funding agencies for failure to support
- Number of experimental installations decays
- Even less ability to deliver

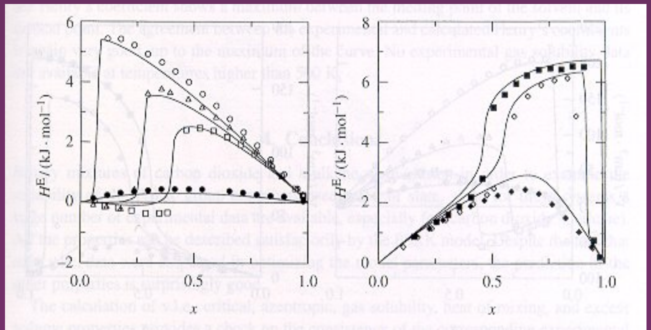


FIGURE 4. Experimental and predicted excess molar enthalpies H^E for $\{xCO_2 + (1-x)C_2H_6\}$; experimental data from Wormald and Hodgetts[22] at $T = 291.6$ K: ●, $p = 3.10$ MPa; ○, $p = 4.00$ MPa; △, $p = 4.88$ MPa; □, $p = 5.40$ MPa; ■, $p = 5.60$ MPa; ◊, $p = 5.85$ MPa; ♦, $p = 6.20$ MPa; —, PSRK.

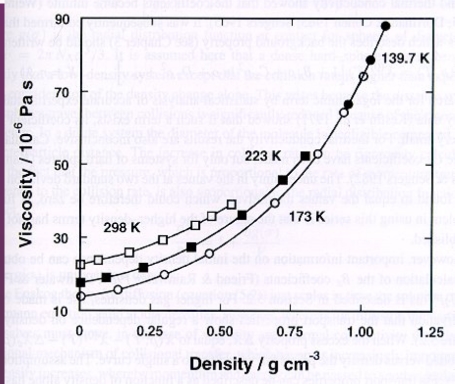


Fig. 5.2. Density dependence of the viscosity of argon.

Reducing experimental activity

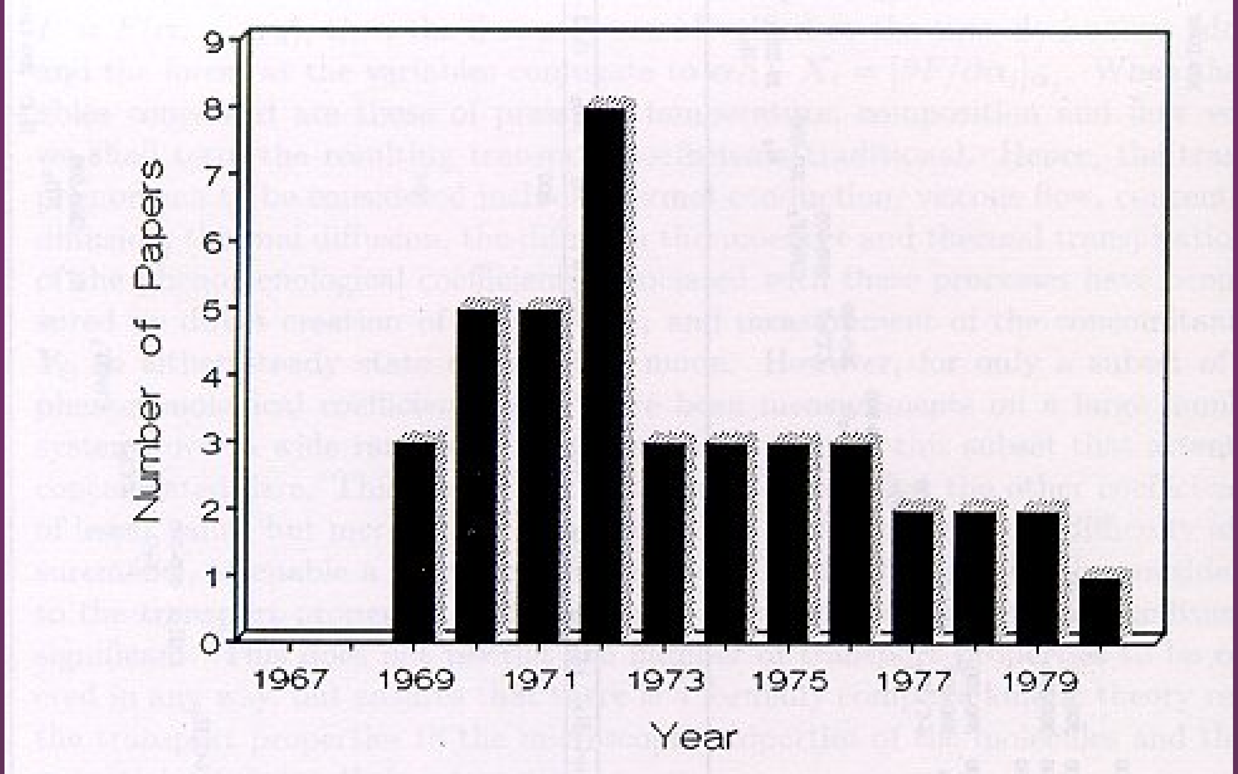
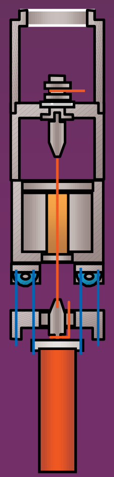
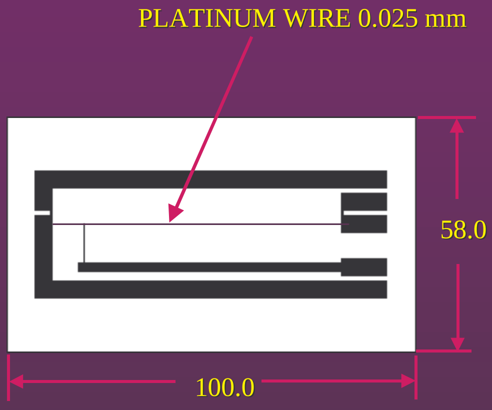


Figure 1. Distribution of viscosity measurements.

Except for a few!

- Imaginative approach to difficult conditions experimentally
  - Molten silicon
  - Molten metals
- Use of new technology to provide accurate and rapid measurement
  - spherical acoustic resonators
  - vibrating-wire viscometer
  - Forced-Rayleigh scattering





Except for a few!

- Critical phenomena - great progress
- A few vital fluid systems studied in focused programmes
- Microgravity

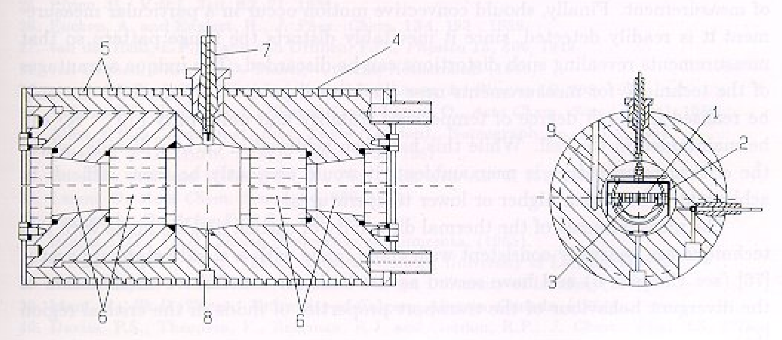


Figure 7.13 The interferometric cell of Becker and Grigull [73-75].

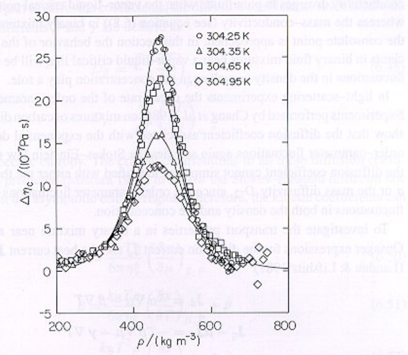


Fig. 6.6. Critical viscosity enhancement $\Delta\eta_c$ of CO_2 deduced from data obtained by Iwasaki and Takahashi (1981). The curves represent calculated values of $\Delta\eta_c$ (Vesovic *et al.* 1990).

Now

- Routine/mundane papers
  - JCT One issue: One new system
  - IJT One issue: No new systems studied
- Repetition of familiar systems
- Declining number of active laboratories
  - growth in southern Europe
- Theory and experiment not in contact
- Engineering and experiment not in contact

Now

- Computer simulation nearer to engineering
  - no limitations on conditions
  - no stated limitations on fluids
  - any mixture can be contemplated
  - molecular design offered
  - What-if’s of synthetic routes possible
- Validation against experiment adequate for purpose
- Theory begins to lose its place
- Is this healthy?

Analysis

- A plateau in the development of the subject of greater length than usual
  - Some of the tasks from earlier divergences have been solved
  - The theoretical tasks that remain have proved exceedingly difficult
    - liquids
    - dense gases
    - non-spherically symmetric molecular systems
    - intermolecular potentials

Analysis

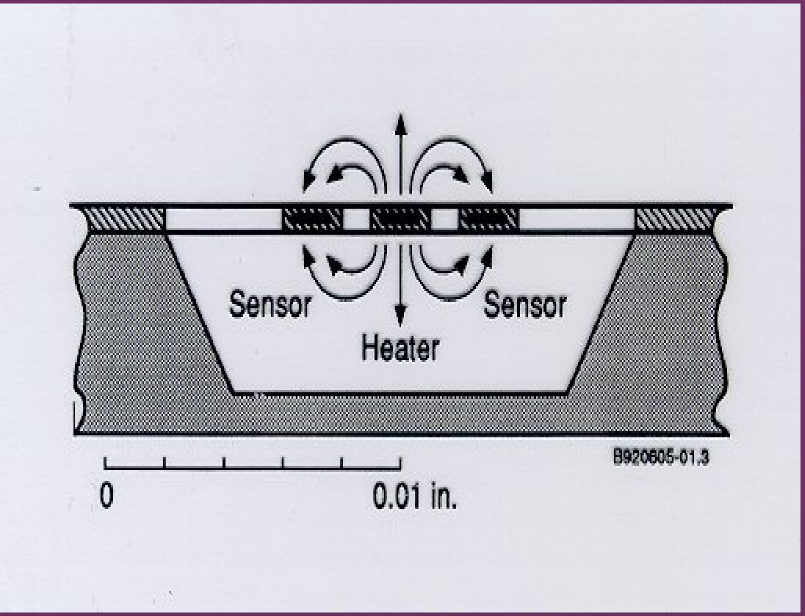
- Experiment for engineering purposes is very difficult
  - High/Low temperature
  - Ill-characterised systems
  - Mixtures
  - Speed
  - Adequate accuracy
  - Integrated with the engineering problem
- Separation from theory makes the subject more like reproduction than sex!
- Increasing direct role of simulation reduces role of /need for theory

Possible ways forward

- Diversify (As a deliberate act)
  - Engineering applications
    - Find real problems where the properties of the fluids matter a great deal. Carry out thermophysical component ***and*** the engineering component
      - Molten silicon
      - Composition distribution in oil reservoirs
      - Reaction injection moulding
      - Chemically-reacting systems

Possible ways forward

- Instrument development
- Use experience of years of development to meet need for adequate accuracy for all systems by design of in-situ measurement capability (sensors)
- New technology offers opportunity
  - micro/nano instruments
- health applications
- process control
- Industrial instruments that produce accurate results without especial care and skill



Possible ways forward

- Rediscover Physics in the field
  - Return to problems neglected that may have an exciting outcome and may now be tractable
    - liquid state of atomic systems
    - monatomic species
    - metals
    - Plasmas
  - Link Experiments with tests of theory not empirical recipes
  - Link Simulation and theory more vigorously
      - Phase behaviour?
  - Moderately dense gases (transport)

Possible ways forward

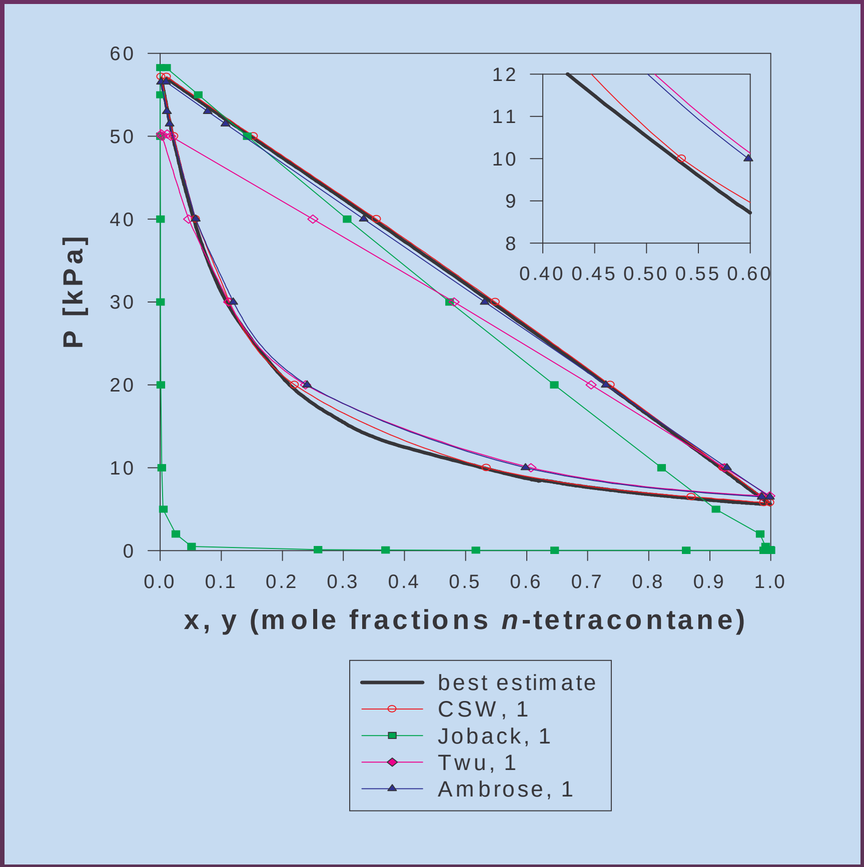
- New materials
  - molten polymers
  - liquid crystals
- Heterogeneous systems
  - Insulations
  - Liquid foams
  - Cells
  - Tissues
- Reacting systems
  - separation and reaction simultaneously

Possible ways forward

- Reclaim Engineering software
  - This field has been surrendered to process/computing engineers with no training in the field of thermophysics
  - Dangerous!

  - Combine the physics with appropriate software
  - Development of robust algorithms
    - Phase equlibrium
    - ***and*** in reacting systems

P-x phase envelopes of the n-eicosylbenzene + n-tetracontane mixture at T = 658 K



Conclusions

- The field is in danger of becoming a dinosaur
  - It must evolve
  - use the pattern that has worked in the past when evolution was needed
- Find real challenges
  - linkages with Physics
  - linkages with Chemistry
  - linkages with Engineering
- Attack new materials and seek to ***explain*** their properties not merely record them